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ASSESSMENT OF PHOTOOXIDATION OF FLEXIBLE PLASTICS
ROOFING BY A COLORIMETRIC METHOD

by

Keith G. Martin

~~Not for publication or
for reference.~~



U.S. DEPARTMENT OF COMMERCE
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investigation of this aspect has therefore been made and at the same time the applicability of a recently developed colorimetric method for measuring photochemical degradation of polyesters [1]² to the types of plastics used in these new roof coverings has been explored.

1.2 Colorimetric Assessment of Photooxidation

Methods of evaluating the changes in plastics due to exposure to solar radiation are usually concerned with changes in visual appearance (color, gloss, light transmittance) or changes in physical properties (tensile strength, extensibility, stiffness, tear strength). Chemical changes are extremely difficult to study since these commercial materials are inherently variable in chemical structure and usually contain a number of additives with high content of functional groups.

It is therefore of considerable interest that a colorimetric method of assessing photochemical degradation has been developed and applied to several classes of plastics [2]. The method is based upon the reaction of a solution of N,N-dimethyl-p-phenylenediamine (DMPDA) with the surface of the exposed plastic. Since photochemical degradation is a surface phenomenon the method is more sensitive than methods of evaluation that concern the complete specimen.

2. EXPERIMENTAL

2.1 Materials Examined

Five liquid-applied coatings and two prefabricated sheet materials were examined. Most of the coatings were applied to strips of glass (3-1/2 X 5/8 X 1/8 in.) by means of a Fisher-Payne dip coater adjusted to give a thickness of .005 to .007 in. When cured, the coatings were removed from the edges and one face of the glass by means of a razor blade and the thickness of the cured coating was checked. An area of coating of approximately 2 sq. in. (3-1/4 X 5/8 in.) was exposed. The types of coatings examined were:

- acrylic emulsion (Ac)
- butyl rubber emulsion (BR)
- chlorsulphonated polyethylene solution (CSP)
- poly(vinyl-chloride-acetate) solution (PVCA)
- and silicone rubber solution (SR).

All coatings were commercial products, but only Ac, CSP, and SR were specially formulated for roofing application. The PVCA coating was clear, and the others were pigmented white.

²Numbers in brackets refer to the list of references at the end of this report.

The flexible sheets examined were:

0.100 in. poly(vinyl-chloride) (PVC), light grey
and .002 in. poly(vinyl-fluoride) (PVC), both clear and white.

These were cut into strips 3-1/4 x 5/8 in. and fixed to the glass supports by means of adhesives. Both materials were commercial products, the former being designed as a flexible roof flashing and the latter as a sheet roofing being fixed with special adhesive to a neoprene-bonded asbestos felt.

2.2 Methods of Exposure

The plastics were exposed to both solar and carbon-arc irradiation.

Solar exposures were carried out by taping the glass supports to aluminum panels which fitted onto outdoor exposure racks. The racks were inclined at 45° to the horizontal facing south and mounted 3-5 feet above a gravel surfaced asphalt roof approximately 350 feet above sea level at Washington, D. C. (lat. 38°57'N, long. 77°05'W). A number of replicates of each specimen were exposed and duplicates were withdrawn after various durations of exposure between August 1963 and June 1964. It is important to note that these outdoor-exposed specimens were not shielded from rain.

Exposures to the carbon arc were carried out with similar specimen holders as used for the outdoor exposures. The aluminum panels were fitted onto the rotating drum of an Atlas single-arc weatherometer, Model SMC-R, so that the specimens faced the arc continuously. The specimens faced the arc continuously. The panels were inverted daily. Exposure to the radiant energy from the enclosed arc was made under a constant black body surface temperature of 140 ±5°F. and the specimens were not subjected to water spray. A set of replicates was exposed and duplicates removed from the weatherometer for examination after various durations of exposure.

Clock time was used to define the exposure durations to the carbon-arc irradiation. This is valid since the intensity of radiant energy on the specimens is approximately constant. According to previous work [3] this intensity is estimated to be 6 langleys/min. compared to a maximum intensity of solar radiation recorded on a surface normal to the solar beam at the above site during midsummer of 1.4 langleys/min. which is equivalent to 1.3 langleys/min. on a surface facing 45°S.

Durations of outdoor exposures were also expressed in clock time. However, since the intensity of solar radiation is continually changing it would have been of more interest to have recorded solar radiation intensity particularly with respect to a series of different ranges of wavelength. As an item of general interest the total hours of sunshine as recorded at Washington National Airport (lat. $38^{\circ}51'N$, long. $77^{\circ}02'W$) have been included.

2.3 Methods of Assessment

Treatment of the irradiated plastics with DMPDA and subsequent evaluation were carried out essentially in accordance with the methods described by Gray and Wright [1, 2]. Solutions used were as follows:

(a) Reagent

0.200 g DMPDA.2HCl was dissolved in 5.0 ml 0.4N potassium hydroxide and immediately diluted with 100 ml methyl alcohol to prevent discoloration, then made up to 200 ml in volumetric flask with benzene to give a reagent concentration of 1.00 mg/ml.

(b) Buffer

25 ml of 0.2 molar potassium acid phthalate was added to 20.3 ml of 0.1N hydrochloric acid and diluted with water to 100 ml in a volumetric flask to give a buffer of pH = 3.0.

(c) Reagent Detector

1.000 g benzoyl peroxide was dissolved in 10 ml benzene and diluted to 100 ml in a volumetric flask with methyl alcohol to give a concentration of 10.0 mg/ml.

A Meeco Tristimulus Color Difference Meter, standardized on the green, red and blue reflectance values of a white glass 90 percent reflectance standard was used to define the color of the plastics. The color of each specimen was defined both before and after exposure to irradiation and before and after treatment with DMPDA. The sample port of the meter was taped with white polyvinylfluoride to reduce its area to a little less than the exposed surface areas of the specimens of plastics. The white 90 percent reflectance standard glass was placed behind each specimen and a heavy black cloth used as a cover to eliminate stray light. Green, red and blue reflectance values were determined, the specimen rotated about 180° and the measurements repeated. Average values were then calculated and corrected to the modified Adams Coordinate System described by Glasser and Troy [4].

After withdrawal from exposure to radiation the specimens had color measurements taken and were then treated with DMPDA. Each of the duplicates of the exposed plastic and a matching pair of unexposed specimens were separately immersed in 15.0 ml of the reagent solution. Special test tubes were used so that the 15 ml of solution would completely cover the plastics. The tubes were stoppered, securely sealed and placed in a mechanical shaker for 2 hours. After removal of the specimen, the content of unreacted DMPDA in the reagent solution was determined.

A 1.0 ml aliquot of the reacted DMPDA solution was added to a 100 ml volumetric flask containing approximately 80 ml of methyl alcohol and 2.0 ml of buffer. After shaking, this solution was reacted with 1.0 ml of the reagent detector and the time that the addition of detector was made was noted. It was found convenient to handle eight specimens at a time and add the detector to the eight reagent aliquots at 1 min. intervals. After shaking and making up to 100 ml the intensity of pink color developed was measured at fixed time intervals after commencement of the reaction. This was done with a Beckman DU manual spectrophotometer by measuring absorbance (A) in 1.0 cm cells at 520μ against methyl alcohol as reference. Readings of A were usually made after 15, 25, 35, and 45 minutes for each of the eight solutions.

The reaction of the DMPDA reagent with the benzoyl peroxide detector was carried out immediately after the 2-hour shaking period (contact between the reagent solution and the plastics specimen). It was observed that the change in color of the reagent solution itself was quite marked when irradiated plastics were in contact with the reagent but not with unexposed specimens. These changes in color of the reagent solutions were not stable and changed with time from yellow brown to green brown. A direct reading of A at 410μ was made on these solutions approximately 1 hour after completion of the shaking.

Preliminary experiments showed that the Ac and BR coatings were swollen and detached from the glass supports by immersion in the DMPDA solution. Gray and Wright [2] used a complete solution technique to overcome this problem, but since this method could not be applied to all the plastics a different approach was used in the present work. The solvent power of the DMPDA solution was reduced by using methyl alcohol only to dissolve the DMPDA for reaction with Ac and BR specimens.

3. RESULTS

3.1 Amount of DMPDA Reagent Reacted

Absorbance of 520μ due to the pink color developed between residual DMPDA reagent solution and detector, gave a similar plot against time in all cases; it rapidly increased to a maximum at 25 to 30 minutes after commencement of reaction, then decreased slowly. A typical set of plots is shown in Figure 1. The procedure adopted was to estimate maximum A at 520μ as the intercept between the straight line joining the first two readings with that joining the final two readings.

Although the reaction between DMPDA and benzoyl peroxide is not completely understood, Gray and Wright [1] have shown that A at 520μ is directly proportional to DMPDA concentration over the range of concentrations of interest. The difference between maximum A at 520μ for the reagent after contact with an unexposed plastics specimen and after contact with an exposed specimen may therefore be taken as an indication of the amount of reagent that reacted with products of photooxidation on the surface of the exposed plastics.

Table 1 gives the mean maximum A at 520μ for the reagent solutions reacted with the detector after contact with specimens exposed outdoors and indicates the equivalent amounts of DMPDA depleted from the reagent solution. Duplicate results were in excellent agreement for these and other measurements made and only means are given in this report.

Table 2 gives similar data for the specimens exposed to carbon-arc irradiation.

It is of interest to note that the maximum A at 520μ values corresponding to DMPDA reagent content after contact with the unexposed specimens varies from 0.428 to 0.464. The concentration of the fresh DMPDA \cdot 2HCl reagent solution was 1 mg per ml and according to Gray and Wright [1] when this is immediately diluted to 1 mg per 100 ml and reacted with benzoyl peroxide a maximum A at 520μ of 0.433 is obtained. It is known that the DMPDA solution decomposes on standing and fresh solutions are prepared each day that the reagent is used. However, it would appear worthwhile to obtain quantitative information on this decomposition rate.

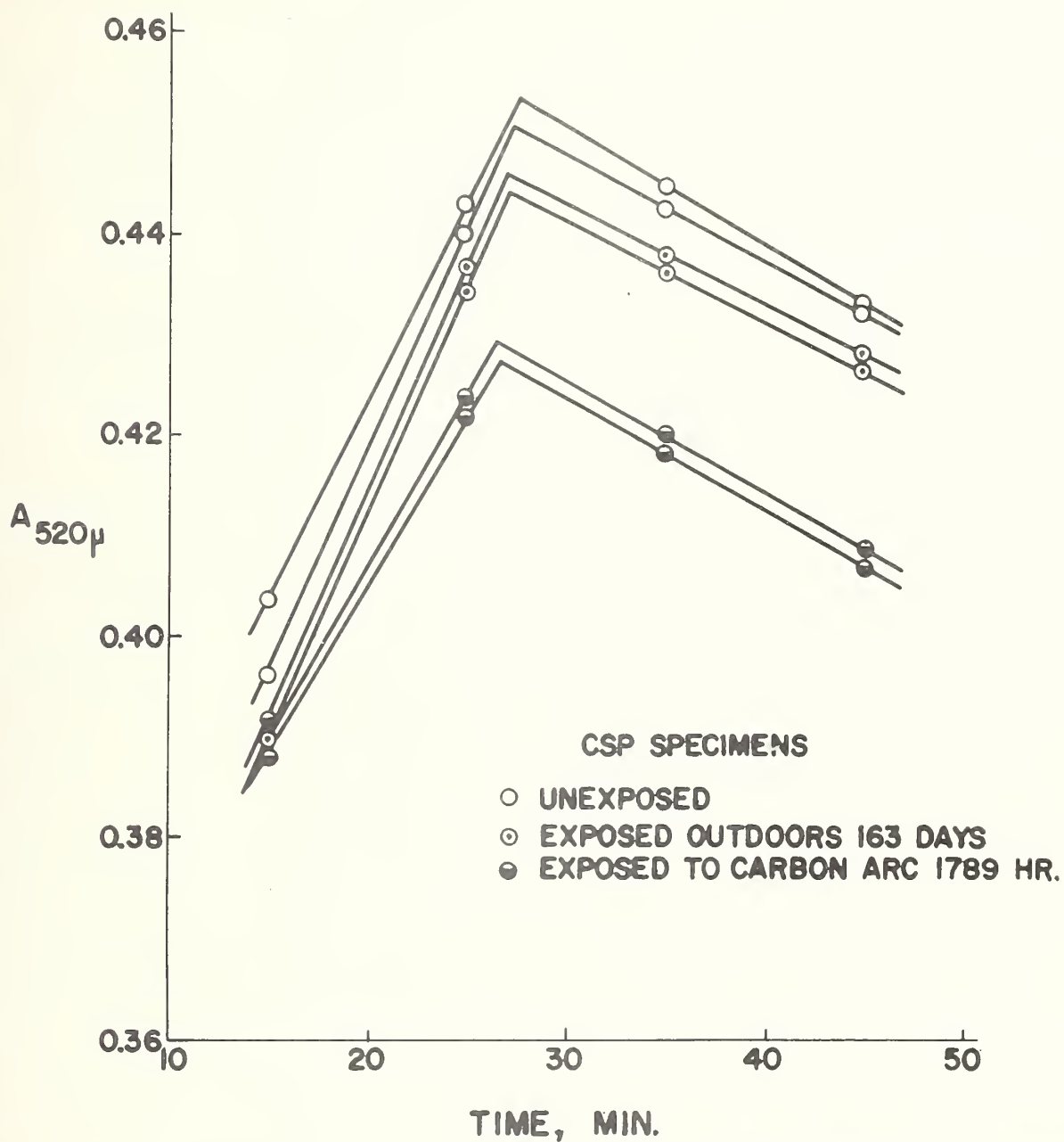


FIGURE 1. TYPICAL ABSORBANCE AT 520μ VERSUS TIME PLOTS FOR RESIDUAL DMPDA REAGENT SOLUTION REACTED WITH BENZOYL PEROXIDE.

TABLE 1. AMOUNT OF DMPDA REACTED WITH SPECIMENS EXPOSED OUTDOORS

SPECIMEN TYPE	EXPOSURE DURATION		MEAN A _{max} AT 520/m		ΔA	DMPDA REACTED (MG.)
	(DAYS)	(SUNSHINE HR)	UNEXPOSED	EXPOSED		
Ac (White)	63	420	.437	.436	.001	.023
	125	947	.429	.424	.005	.114
BR (Off-white)	51	352	.440	.405	.035	.798
	163	1145	.429	.420	.009	.205
	233	1614	.440	.432	.008	.182
	295	2141	.436	.430	.006	.137
OSP (White)	51	352	.456	.453	.003	.068
	163	1145	.452	.445	.007	.160
	233	1614	.456	.448	.008	.182
	295	2141	.454	.439	.015	.342
PVCA (Clear)	51	352	.446	.442	.004	.091
	163	1145	.439	.429	.010	.228
SR (White)	63	420	.450	.450	Nil	Nil
	125	947	.449	.460	-	-
PVC (Grey)	63	420	.428	.410	.018	.410
	125	947	.428	.420	.008	.182
PVF (White)	233	1614	.442	.439	.003	.068
	295	2141	.442	.437	.005	.114
PVF (Clear)	233	1614	.436	.435	.001	.023
	295	2141	.442	.436	.006	.137

TABLE 2. AMOUNT OF DLPDA REACTED WITH CARBON-ARC IRRADIATED SPECIMENS

SPECIMEN TYPE	EXPOSURE DURATION (hr.)	MEAN A _{max} AT 520/ μ		Δ A	DLPDA REACTED (mg.)
		UNEXPOSED	EXPOSED		
Ac (white)	1517	.429	.422	.007	.160
BR (off white)	723	.429	.425	.004	.091
	1789	.429	.417	.012	.274
	2742	.440	.428	.012	.274
	3549	.436	.418	.018	.410
CSP (white)	106	.464	.452	.012	.274
	245	.454	.438	.016	.365
	449	.454	.432	.022	.502
	723	.462	.439	.023	.524
	1789	.452	.428	.024	.547
	2742	.456	.414	.032	.730
PVCA (clear)	106	.454	.447	.007	.160
	245	.454	.442	.012	.274
	449	.445	.431	.014	.319
	723	.439	.418	.021	.478
	1083	.454	.424	.030	.684
SR (white)	320	.450	.450	nil	nil
	610	.450	.450	nil	nil
	1517	.449	.446	.003	.068
PVC (grey)	320	.428	.423	.005	.114
	1517	.428	.414	.014	.319
PVF (white)	1084	.445	.440	.005	.114
	2742	.445	.435	.010	.228
	3549	.442	.429	.013	.296
PVF (clear)	1084	.444	.440	.004	.091
	2742	.436	.430	.006	.137
	3549	.442	.433	.009	.205

3.2 Color Developed in DMPDA Reagent Solution

Proper attention was not given to the measurement of color developed in the DMPDA reagent solution due to contact with exposed plastics because the determination of DMPDA content by reaction with benzoyl peroxide was believed to be the better method of assessing the depletion of DMPDA. The colored solutions were unstable, some changing more rapidly than others. However, some absorbances at 410μ determined approximately one hour after completion of the 2-hour shaking period are given in Table 3.

Phenylenediamines are well known as reagents to detect the presence of peroxides which, if present, give a characteristic pink color to the solution. No such color was observed when most of the exposed plastics were immersed in the DMPDA solution. However, part way through the project the technique was slightly altered and several drops of the DMPDA solution were placed on the surfaces of the exposed plastics before immersing the specimen completely in DMPDA. In many cases the characteristic pink color developed immediately indicating the presence of peroxides on the surface of the plastics. It generally persisted for a few minutes only. The plastics surfaces on which peroxides were thus detected are indicated in Table 3.

3.3 Color Developed on Specimen Surface

The color that developed on the exposed plastics surfaces after the specimens were shaken in the DMPDA reagent solution were very stable and changed little in storage after several weeks. Tristimulus reflection measurements were usually taken on dry specimens 1 day after the immersion in the DMPDA reagent.

Some changes in color occurred when unexposed specimens were immersed, but were usually much less than that induced with the exposed specimens.

Table 4 gives the Adams coordinates for the unexposed untreated specimens and the unexposed DMPDA-immersed specimens together with the differences which may be attributed to reaction between the reagent and the unexposed plastics. Where clear plastics were measured, the determinations depend upon the white 90 percent reflectance standard glass used as a backing.

Table 5 gives the changes in Adams coordinates due to the outdoor exposure both for the untreated surface (differences between exposed and unexposed specimens) and the DMPDA-treated surfaces (differences between exposed DMPDA-treated and unexposed DMPDA-treated specimens).

TABLE 3. AMOUNT OF COLOR DEVELOPED IN DMPDA REAGENT SOLUTION

SPECIMEN TYPE	OUTDOOR EXPOSURE			CARBON-ARC IRRADIATION	
	DURATION (DAYS)	(SUNSHINE Hr.)	ΔA at 410 μ	DURATION (hr.)	ΔA at 410 μ
Ac (white)	63	420	.028 _P	1517	.175 ^P
	125	947	.085 _P		
BR (off white)	51	352	.007 _P	723	.094
	163	1145	.106 _P	1789	.154 _P
	233	1614	.115 _P	2742	.295 _P
	295	2141	.060 _P	3649	.645 _P
CSP (white)	51	352	.052	106	.210
	163	1145	.210	245	-
	233	1614	.097 _N	449	.250
	295	2141	.250 _N	723	.215
				1789	.382 _P
				2742	.530 _P
PVCA (clear)	51	352	.133	106	.148
	163	1145	.249	449	.431
				723	.602
				1083	.696
SR (white)	63	420	.11 _P	320	Nil
	125	947	.075 _P	610	.002 _N
				1517	.014 _N
PVC (grey)	63	420	.045	320	.160
	125	947	.280	1517	.300
PVF (white)	233	1614	.007 _N	2742	.480 ^P
	295	2141	.012 _N	3649	.470 _P
PVF (clear)	233	1614	.012 _N	1084	.310 _P
	295	2141	.033 _N	2742	.495 _P
				3649	.432 _P

P = Peroxides detected

N = Peroxides not detected.

TABLE 4. COLOR CHANGES DUE TO TREATMENT OF UNEXPOSED SPECIMENS WITH DMPDA REAGENT

SPECIMEN	MEAN FOR UNTREATED			MEAN FOR TREATED			CHANGE		
	L	a	b	L	a	b	ΔL	Δa	Δb
Ac (white)	95.93	-0.5	+3.1	95.00	-1.0	+5.9	-0.93	-0.5	+2.8
BR (off-white)	85.28	-0.7	+3.7	83.28	-1.3	+7.9	-2.00	-0.6	+4.2
GSP (white)	95.36	+0.3	+1.8	94.13	+0.3	+2.5	-1.23	0	+0.7
PVCA (clear)	88.99	-2.9	+1.2	87.38	-3.2	+4.2	-1.61	-0.3	+3.0
SR (white)	97.24	-0.2	+0.2	92.89	-0.2	+0.1	-4.35	0	-0.1
PVC (grey)	81.51	-0.6	+2.0	78.58	+0.3	+5.3	-2.93	+0.7	+3.3
PVF (white)	89.50	+0.4	-1.3	88.77	+0.2	-0.5	-0.73	-0.2	+0.8
PVF (clear)	91.19	+0.1	+1.6	90.80	-0.3	+2.6	-0.39	-0.4	+1.0

TABLE 5. SPECIMEN COLOR CHANGES* DUE TO OUTDOOR EXPOSURE

SPECIMEN	EXPOSURE DURATION		UNTREATED			DMPDA TREATED		
	(DAYS)	(SUNSHINE) (hr.)	ΔL	Δa	Δb	ΔL	Δa	Δb
Ac (white)	63	420	-1.43	-0.7	-0.5	-4.00	+0.4	+1.6
	125	947	-3.71	+1.2	-0.6	-4.18	+0.2	+3.9
BR (off-white)	51	352	-0.39	+0.4	+1.8	-10.65	-0.5	-1.0
	163	1145	-2.73	+1.0	+2.1	-12.26	+1.0	-3.3
	233	1614	-4.97	+1.1	+2.5	-11.95	+1.8	-1.4
	295	2141	-5.59	+1.4	+2.0	-14.41	+0.3	-4.1
CSP (white)	51	352	-2.14	-1.1	+5.4	-5.48	-1.3	+13.5
	163	1145	-1.00	-0.7	+5.2	-5.54	-0.6	+13.3
	233	1614	-0.86	-1.3	+5.2	-6.30	+1.1	+12.4
	295	2141	-0.38	-0.8	+4.6	-10.24	+1.5	+10.3
PVCA (clear)	51	352	-3.22	+0.2	+2.0	-4.68	+0.5	+6.5
	163	1145	-4.53	-1.0	+2.8	-10.59	+2.3	+26.0
SR (white)	63	420	-0.45	-0.1	+0.2	-1.17	-0.3	+0.7
	125	947	-1.47	+0.3	+1.0	-5.62	+0.3	+0.7
PVC (grey)	63	420	-1.21	+0.1	+1.3	-4.90	+0.2	+5.7
	125	947	-1.91	-0.3	+3.0	-7.61	-1.0	+9.0
PVF (white)	233	1614	-0.61	+0.2	-10.1	-1.09	+0.9	+0.1
	295	2141	-1.08	+0.1	+0.3	-1.53	+0.3	+1.0
PVF (clear)	233	1614	-0.36	-0.6	+1.5	-1.45	+1.1	+0.5
	295	2141	-1.86	+1.1	+1.0	-1.93	+0.3	+3.3

*Color changes expressed as changes in Adams Coordinate System with respect to untreated and treated unexposed replicate specimens.

ΔL ; + = lighter, - = darker

Δa ; + = redder, - = greener

Δb ; + = yellower, - = bluer

Table 6 gives similar results for the carbon-arc irradiated specimens.

As mentioned previously, the specimens were smaller than the exposure port of the reflectance meter, so that even a black specimen would register an L value. A matt black surface was measured and gave coordinates of $L = 31.85$, $a = 1.7$, and $b = 2.2$. Considered in relation to the results in Tables 4, 5, and 6, this means that the maximum ΔL value possible is about -60.

4. DISCUSSION

4.1 Outdoor Exposures; Assessment of DMPDA Reaction

Considering the specimens exposed outdoors, the results in Tables 1, 3, and 5 show that three parameters, the amount of DMPDA reacted, the ΔA at 410μ of the reagent solution after DMPDA reaction, and the darkening ($-\Delta L$) of the specimen surface after DMPDA reaction, generally increase steadily with increase of duration of exposure. The increases are not as smooth as those found for polyesters [1,2] and the amount of DMPDA reacted does not increase with exposure time for all specimens, anomalous results being obtained for BR, SR, and PVC. In each of these materials considerable reaction had taken place between DMPDA reagent and the unexposed plastics as shown in Table 4. This reaction is possibly an indication of residual free radical polymerization agents in the plastics.

The two synthetic rubbers after exposure gave pronounced peroxide reactions. Gray and Wright [5] indicate that the DMPDA reagent reacts with certain α, β -dicarbonyl compounds such as α -keto acids, glyoxal and pyruvic aldehyde. Peroxides are generally considered to be precursors of the carbonyl compounds but due to their rapid decomposition little evidence of their presence has been reported or expected. The fact that certain plastics do develop comparatively stable peroxides on their surface is of considerable interest and may explain the greater than usual reaction with DMPDA for these specimens.

Figure 2 illustrates the progressive photooxidation of the surface of the plastics due to outdoor exposure according to the three methods of assessment. The anomalous values for the amount of DMPDA reacted have not been included and the separate results for clear and white PVF have not been distinguished. Each of the three methods of assessment of the reaction between DMPDA and the photooxidized plastics surface has given similar relative results for PVF, Ac, CSP, and PVCA. This indicates that the determination of DMPDA in the reagent solution after the reaction may be unnecessary and that the simpler measurements ΔA at 410μ of reagent solution and tristimulus reflectance of specimen surface may be adequate. However, further studies should be made to determine the influence of plastics

TABLE 6. SPECIMEN COLOUR CHANGES* DUE TO CARBON-ARC IRRADIATION

SPECIMEN	EXPOSURE DURATION (hr.)	UNTREATED			TREATED		
		ΔL	Δa	Δb	ΔL	Δa	Δb
Ac (white)	320	-0.68	-2.3	-0.6	-	-	-
	610	-1.19	+0.5	-0.7	-3.77	+1.1	-0.8
	1517	-7.09	-1.5	+2.2	-12.64	+1.7	+0.9
BR (off-white)	723	+3.33	-1.5	+1.2	-8.96	+0.4	-0.9
	1789	+2.16	0.0	+0.7	-9.77	+0.7	-2.7
	2742	+1.31	0.0	+4.5	-11.31	+0.7	+0.2
	3649	+0.83	-0.5	+3.9	-12.08	+1.6	-1.2
CSP (white)	106	-5.64	-1.9	+22.8	-16.35	+3.0	+24.0
	245	-7.20	+0.6	+28.4	-17.70	+6.1	+17.2
	449	-6.54	-0.6	+19.2	-17.01	+4.6	+11.0
	723	-6.72	+0.5	+18.5	-16.51	+2.3	+8.0
	1789	-6.82	+0.9	+14.7	-16.60	+2.5	+6.4
	2742	-9.48	0.0	+15.5	-19.46	+3.9	+6.0
PVCA (clear)	106	-2.20	+0.5	+2.8	-10.26	+3.0	+21.5
	245	-4.75	+1.5	+6.1	-21.89	+11.8	+23.4
	449	-8.83	+3.9	+7.4	-23.72	+13.0	+25.5
	723	-42.60	+17.3	+9.2	-43.92	+17.9	+8.9
	1083	-53.80	+11.0	+3.5	-50.22	+15.2	+4.7
SR (white)	320	-0.06	-0.2	0	-0.44	+0.2	+0.4
	610	-1.17	-0.3	+0.6	-1.85	+0.2	+0.6
	1517	-1.35	+0.3	+1.0	-5.08	+0.9	+0.1
PVC (grey)	320	-1.10	-1.0	+2.7	-2.95	-0.5	+4.3
	1517	-2.23	-0.3	+3.9	-5.87	-1.3	+4.4
PVF (white)	1084	-	-	-	-	-	-
	2742	-1.21	-0.3	+1.7	-2.38	+0.1	+2.0
	3649	-2.47	-1.5	+1.7	-3.89	-0.8	+5.0
PVF (clear)	1084	-1.34	-1.5	+0.2	-2.23	-0.8	+0.4
	2742	-1.76	-0.5	+1.9	-2.53	+1.1	+2.2
	3649	-1.97	+0.1	+2.5	-3.82	-0.3	+2.1

*Color changes expressed as changes in Adams Coordinate System with respect to untreated and treated unexposed specimens.

ΔL ; + = lighter, - = darker

Δa ; + = redder, - = greener

Δb ; + = yellower, - = bluer

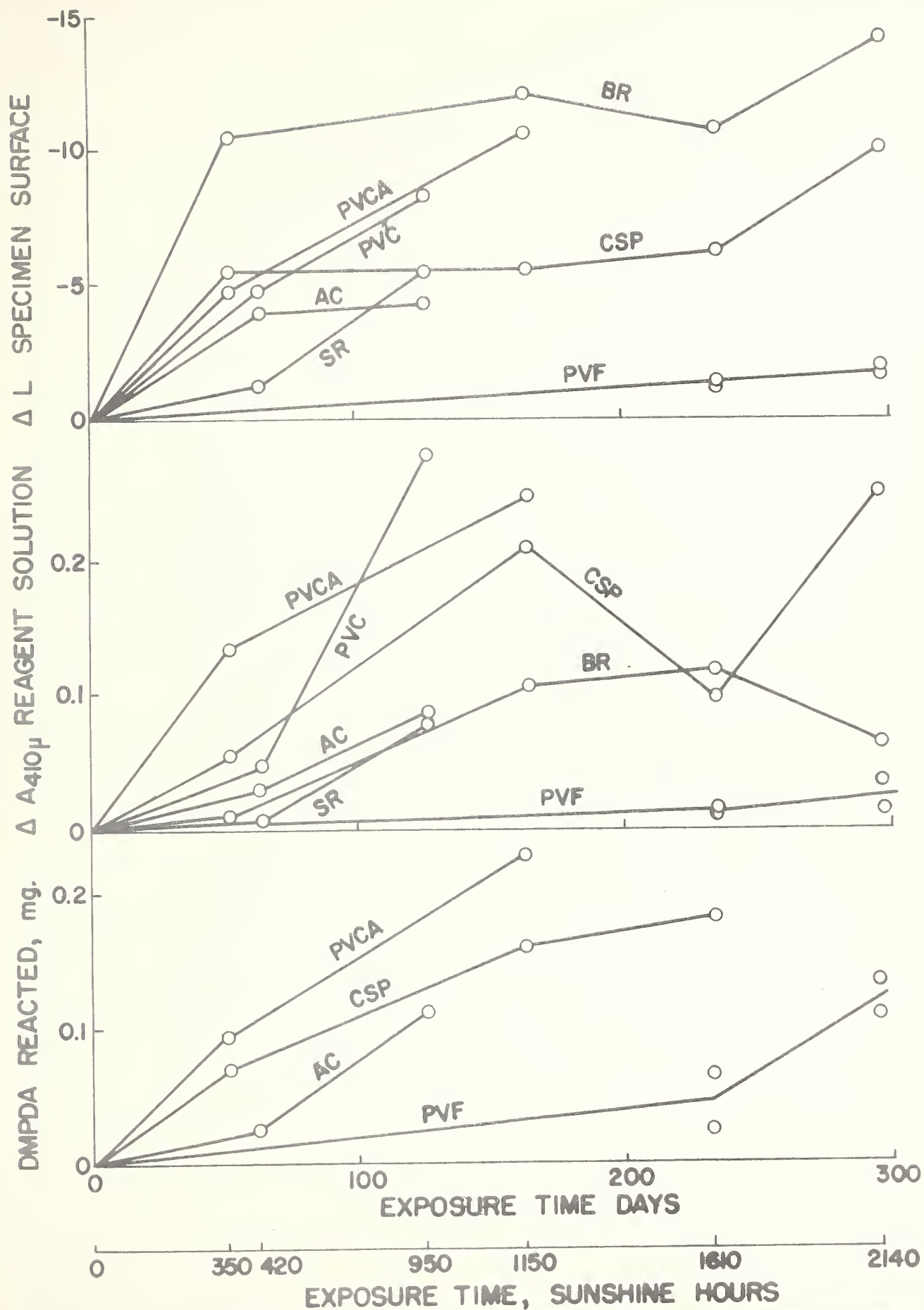


FIGURE 2. PROGRESSIVE PHOTOOXIDATION OF SPECIMENS EXPOSED OUTDOORS, ACCORDING TO THE DMPDA REACTION.

type upon the absorption spectra in the visible region of the reagent solution after reaction and also to obtain quantitative data on the stability of the colored solutions and repeatability of the method.

The SR and PVC specimens have given similar results for both darkening ($-\Delta L$) of treated plastic surface and ΔA at 410μ of reagent solution after reaction of exposed samples with DMPDA. Only the BR results are not in agreement for these two methods of assessment.

4.2 Outdoor Exposure; Changes in Color of Untreated Specimens

Darkening of the plastics due to outdoor exposure without any DMPDA treatment generally increases regularly with increase of exposure time and is illustrated in Figure 3. Comparison to Figure 2 shows a similar relative assessment for specimens PVF, SR, Ac, CSP, and PVCA except that the CSP gets lighter in color after about 50 days of exposure and this is not paralleled by assessment of DMPDA reaction with the surface. It is of interest to note that the darkening of the untreated surface ranks the BR in the same position as does the ΔA at 410μ of the reagent solution after DMPDA reaction with the exposed surface. However, this may be fortuitous since the BR surface picked up considerable grime due to outdoor exposure and could not be completely washed clean. Darkening of the untreated PVC is less than expected on the basis of a correlation between results in Figures 2 and 3. This may be explained by the initial grey color of the PVC flexible sheet tending to mask the color change due to exposure.

Yellowing ($+b$ coordinate in table 5) has not increased regularly with duration of outdoor exposure for the untreated surfaces and only darkening ($-\Delta L$) is a useful parameter for evaluating the visual changes in color of the plastics due to outdoor exposure.

4.3 Carbon-arc Exposures; Assessment of DMPDA Reaction

Each of the assessments of the DMPDA reaction with the carbon-arc irradiated plastics (Tables 2, 3, and 6) has increased with increase of exposure duration as illustrated in Figure 4. The ranking of the various plastics surfaces is similar for the three modes of assessment except in two cases. The ΔA values at 410μ of reagent solutions for the PVF specimens were abnormally high, but at present an explanation of this result cannot be made. The other result that is not in general agreement is the darkening ($-\Delta L$) of the treated PVC surface which has been discussed previously.

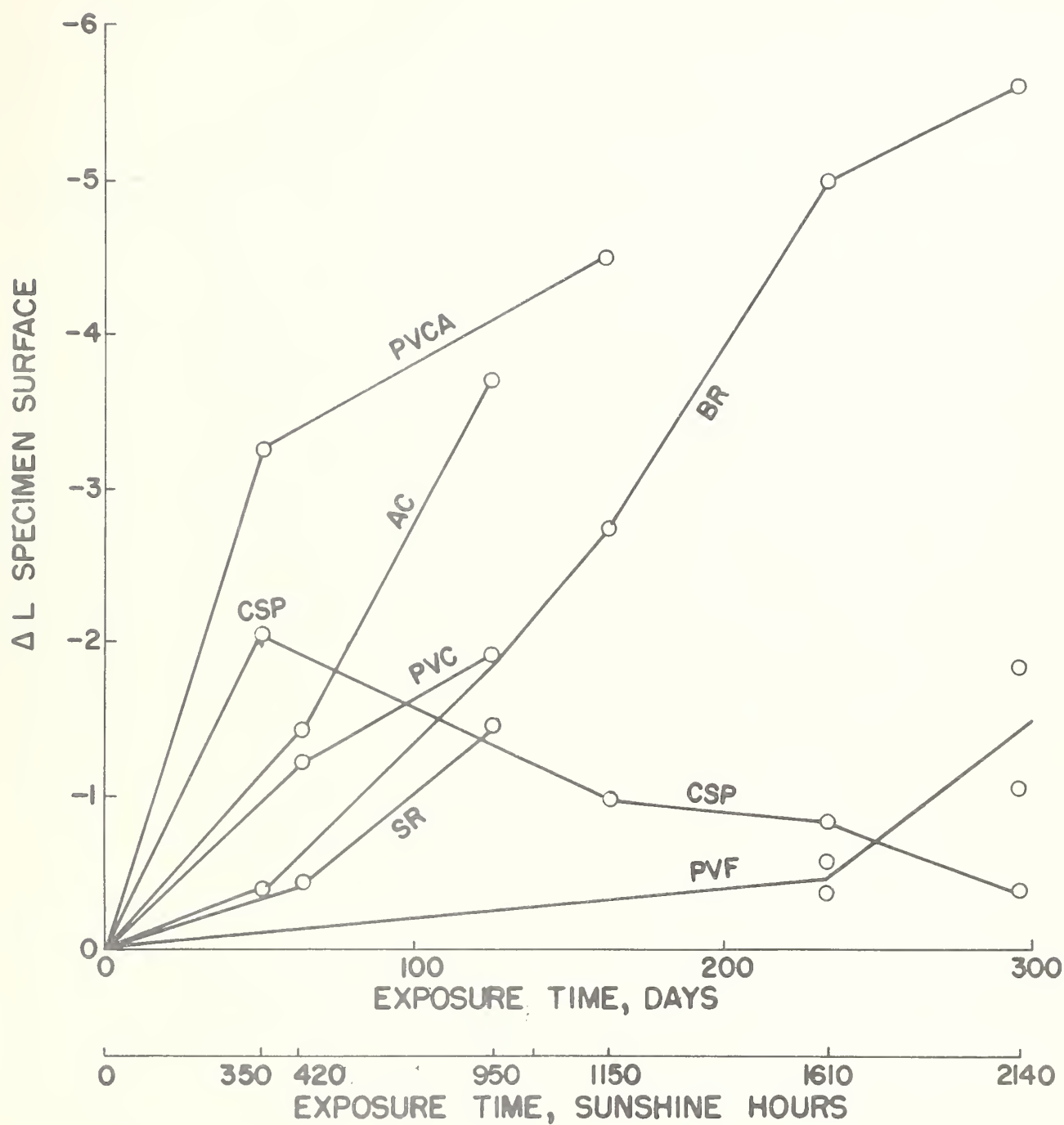


FIGURE 3. PROGRESSIVE DARKENING OF SPECIMENS DUE TO OUTDOOR EXPOSURE ONLY.

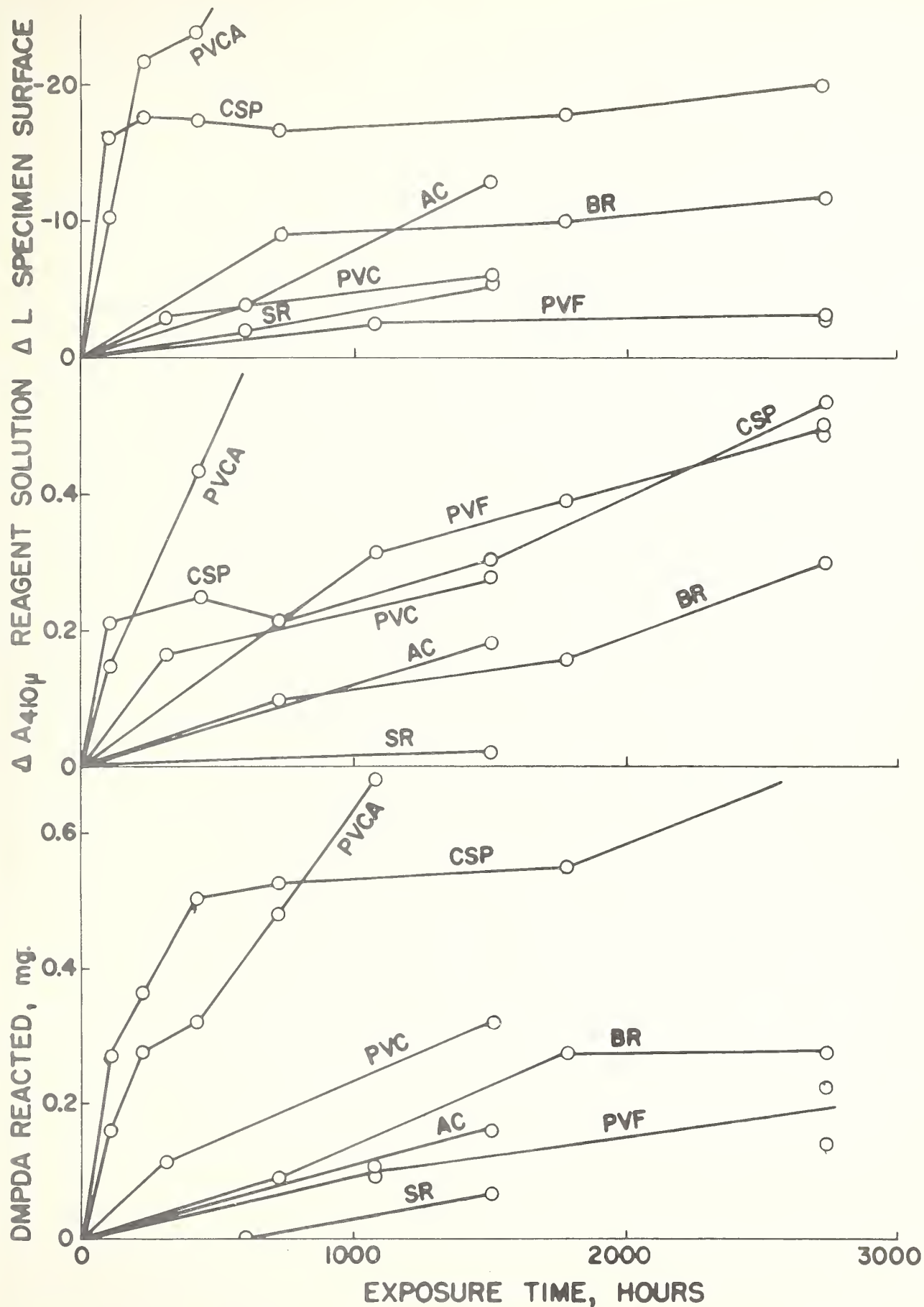


FIGURE 4. PROGRESSIVE PHOTOOXIDATION OF SPECIMENS EXPOSED TO CARBON-ARC IRRADIATION, ACCORDING TO THE DMPDA REACTION.

It is worthy of note that none of the determinations of DMPDA reacted has given apparent anomalous results despite the fact that peroxides were detected on most of the surfaces irradiated.

4.4 Carbon-arc Exposures; Changes in Color of Untreated Specimens

Figure 5 illustrates the progressive darkening ($-\Delta L$) (table 6) of the plastics irradiated with the carbon-arc. Results for BR are unusual since a short duration of exposure has caused the surface to become lighter and further subsequent exposure has then induced darkening. Comparison of Figure 5 to Figure 4 shows a similar ranking of the different plastics to that given by the DMPDA reaction.

Yellowing of these plastics ($+\Delta b$, table 6) shows a regular change for most specimens. In several cases (BR, CSP, and PVCA) yellowing passes through a maximum. As found for outdoor exposures, only darkening ($-\Delta L$) is a useful parameter for evaluating the visual color changes of the different plastics due to irradiation.

4.5 Comparison of Performance of Materials

Although further work needs to be done concerning the validity of using the DMPDA reaction as a method for comparing the relative photochemical stabilities of different types of plastics, an apparent applicability to a wide range of plastics has been established in this work. On the basis of the four methods of assessment, the general rankings found for the plastics are indicated in Table 7. The general order for outdoor exposure beginning with the least stable is:

PVCA
PVC
CSP
Ac
SR
PVF

the relative ranking of BR being not clear.

The general order for stability to carbon-arc irradiation beginning with the least stable is:

PVCA
CSP
PVC
BR
Ac
PVF
SR

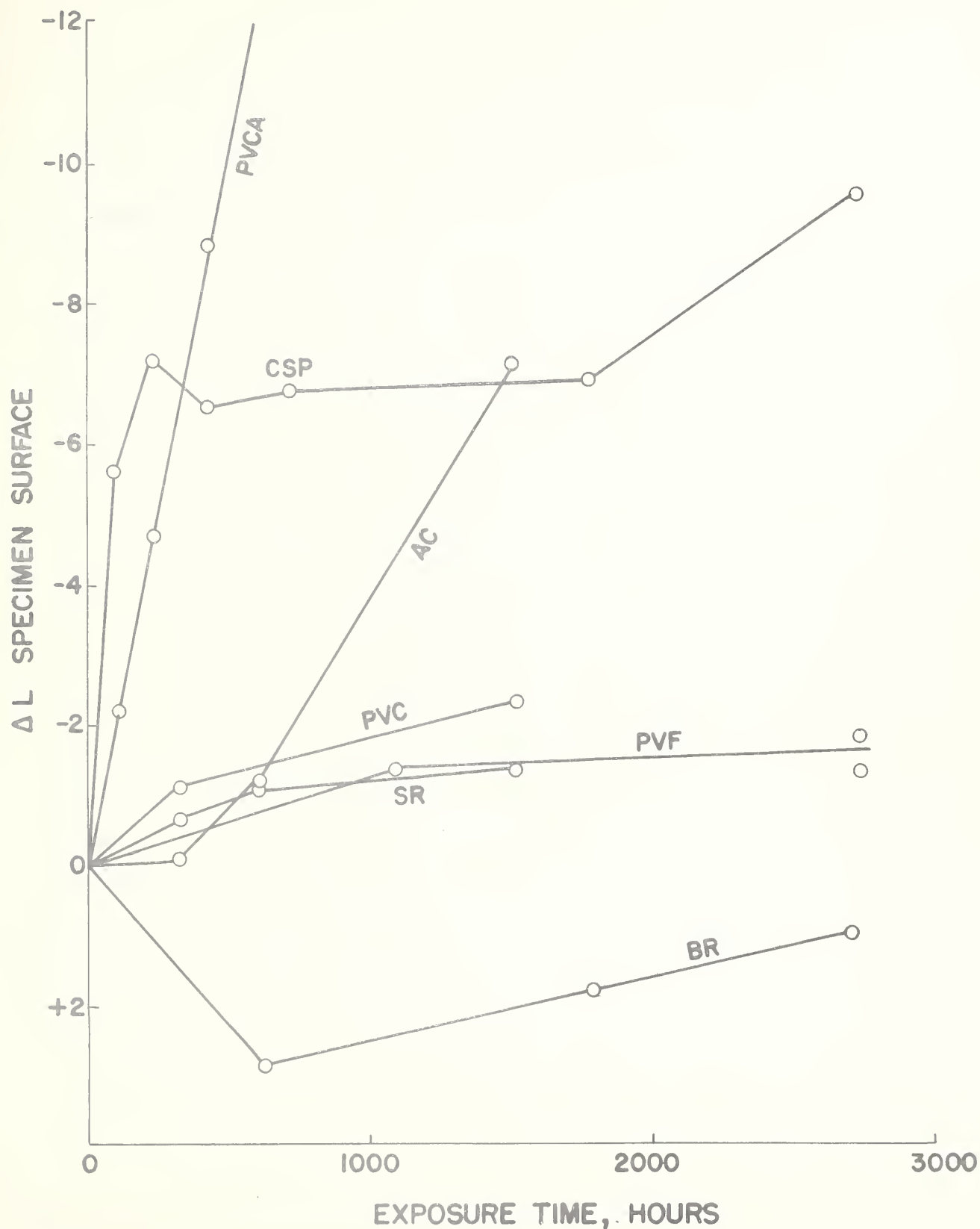


FIGURE 5. PROGRESSIVE DARKENING OF SPECIMENS DUE TO CARBON-ARC IRRADIATION ONLY.

TABLE 7. INCREASING ORDER OF PHOTOCHEMICAL STABILITY OF THE FLEXIBLE PLASTICS

METHOD OF ASSESSMENT			
DMPDA TREATED			UNTREATED
DMPDA REACTED	$\Delta A_{410\mu}$ REAGENT SOLUTION	$-\Delta L$ SPECIMEN SURFACE	$-\Delta L$ SPECIMEN SURFACE
<u>Outdoor Exposures</u>			
		BR	
PVCA	PVCA	PVCA	PVCA
	PVC	PVC	
CSP	CSP	CSP	CSP
Ac	Ac	Ac	Ac
			PVC
	BR		BR
	SR	SR	SR
PVF	PVF	PVF	PVF
<u>Carbon-arc Exposures</u>			
PVCA	PVCA	PVCA	PVCA
CSP	CSP	CSP	CSP
	PVF		
PVC	PVC		
BR	BR	BR	
Ac	Ac	Ac	Ac
		PVC	PVC
		SR	
PVF		PVF	PVF
SR	SR		SR

4.6 Comparison of Effects of Different Exposures

Apart from the anomalies previously discussed, there are a few differences between the effects induced in the plastics by the different exposure conditions. A comparison of the performance of the different plastics as shown in Figures 2 and 4 does indicate that PVCA is more labile when irradiated with the carbon arc than with natural sunlight. The CSP specimens also show during initial carbon-arc irradiation, a relatively rapid reaction. On the other hand, the SR specimens appear to be relatively more stable to the carbon arc than to outdoor exposure. It is not possible to discuss these observations at this stage since there are at least four important differences between the methods of exposure, viz:

- (a) the spectral energy characteristics of the sources of radiant energy;
- (b) the intensities of the radiant energy falling on the specimens;
- (c) the surface temperatures of the specimens;
- (d) the presence of water on the specimens.

It may be noted however that the carbon-arc irradiated specimens have degraded only about twice as fast as the specimens exposed outdoors when considering the hours of irradiation received. As discussed previously, the average intensity of solar radiation would be at least ten times less than the radiation impinging on the specimens in the carbon arc.

Another point of interest is that peroxides were detected on the surfaces of CSP and PVF exposed to carbon-arc irradiation, but not when exposed outdoors (Table 3). The opposite behavior was observed for SR, peroxides being detected on an outdoor exposed specimen, but not on a specimen irradiated with the carbon arc. These observations appear to be associated with the extent of photooxidation of the surfaces. Both the CSP and PVF specimens were degraded to a greater extent in the carbon arc than when exposed outdoors; whereas the SR was degraded further in the outdoors exposure according to the methods of assessment employed.

5. CONCLUSIONS

1. A wide range of types of organic polymers and elastomers form photo-oxidation products on their surfaces which react with DMPDA. Samples, mostly commercial products of the following roofing materials, have shown little reaction with DMPDA when treated as unexposed specimens and considerable reaction when specimens that had been exposed outdoors or irradiated with the carbon arc were treated:

acrylic, butyl-rubber, chlorsulphonated-polyethylene,
poly(vinyl-chloride-acetate) and silicone rubber coatings,
poly(vinyl-chloride) and poly(vinyl fluoride) flexible sheets.

Other workers [2] had shown similar reactions with rigid polyesters, poly(vinyl-chloride), poly(methyl-methacrylate) and cellulose-acetate-butyrate.

2. Quantitatively, the reaction with the flexible materials does not appear to be as repeatable as when applied to the rigid materials. Three methods were found to be useful for assessing the extent of the DMPDA reaction with a photooxidized surface, viz:

- (a) determination of depletion of DMPDA by colorimetric detection with benzoyl peroxide;
- (b) measurement of color developed in the DMPDA reagent solution (A at 410μ);
- (c) measurement of darkening of specimen surface (Adams coordinate $-\Delta L$).

Apart from some anomalies which necessitate further investigation, good agreement was found between the ranking of the different materials by the different methods of assessment.

3. The assessments of the reaction with DMPDA gave results that generally agreed with the amount of darkening (Adams coordinate $-\Delta L$) caused by exposure only.

4. The DMPDA reaction offers considerable promise as a means of assessing the relative stability to photooxidation of different types of organic polymers and elastomers after comparatively short periods of exposure. The roofings examined in this work were generally rated in the following

order beginning with the least stable:

- poly(vinyl-chloride-acetate) coating
- poly(vinyl-chloride) sheet
- chlorsulphonated-polyethylene coating
- butyl-rubber coating
- acrylic coating
- silicone-rubber coating
- poly(vinyl-fluoride) sheet

Some differences in this order were found for the different methods of assessment and according to whether the materials were exposed outdoors or to the irradiation of the carbon arc.

5. Peroxides may be detected on the surfaces of photooxidized polymers and elastomers by the application of several drops of DMPDA solution to the surface and observing the development of a pink color.

6. ACKNOWLEDGMENT

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